EFFECT OF ANHARMONICITY ON THE THERMODYNAMIC BEHAVIOUR OF A SOLID

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ABSTRACT. A method is suggested, to take into account the effect of anharmonicity on the thermodynamic functions, in a temperature range where quantum effects are important. Expressions for the Gibb's function G and the specific heat at constant pressure C_p are deduced for a simple model of a solid. These results reduce to the well known classical expressions in the limit of high temperatures.

INTRODUCTION

Much work has been done (Born, 1939, 1943; Bradburn, 1943; Dugdale and MacDonald, 1954) about the role of the anharmonic terms in the potential energy on the thermodynamic properties of solids at high temperatures. A term linear in temperature, occurs in the specific heat of a solid at high temperatures (Peierls, 1955; Leibfried, 1955) due to this.

The influence of anharmonicity in the temperature range where quantum effects are significant, has not been considered in a logical way. Stern (1957) after developing the whole theory classically, replaces $3R$ by $3R.F(\theta/T)$ in the end, where F is the Debye function, as a first factor in the specific heat C'_p of an anharmonic solid. It tells only a part of the story and is incomplete in its development from the quantum point of view.

In the following, first a general formulation of the quantum mechanical thermodynamic perturbation theory (Landau and Lifshitz, S. M., 1958) is given. It is then applied to a model of a solid, to arrive at the expressions for the Gibb's function G and the specific heat at constant pressure C'_p. In the end it is shown that this gives the correct expression for the specific heat at high temperatures.

GENERAL FORMULATION

The partition function at constant pressure, Q when E_n are the energy eigen values of the system, is given by,

$$Q = \sum_n e^{-E_n/kT} \qquad \ldots \quad (1)$$

The energy eigen levels E_n of the perturbed system, using quantum perturbation theory up to second-order corrections are,

$$E_n = E_n^0 + V_{nn} + \sum_m' \frac{|V|^2}{(E_n^0 - E_m^0)}$$

$$= E_n^0 + E_n^1 + E_n^2 \qquad \ldots (2)$$

where E_n^0 are the unperturbed energy levels and E_n^1 and E_n^2 are the 1st- and 2nd- order corrections due to the perturbing potential V.

The condition for the validity of the quantum pertur tion theory i.e. $|V_{mn}| << |E_n^0 - E_m^0|$ is assumed.

Substituting (2) in (1),

$$Q = \sum_n e^{-E_n/kT}$$

$$= \sum_n e^{-E_n^0/kT} \cdot e^{-(E_n^1 + E_n^2)/kT}$$

$$= \sum_n e^{-E_n^0/kT} \cdot \left[1 - \frac{(E_n^1 + E_n^2)}{kT} + \frac{(E_n^1 + E_n^2)^2}{2k^2T^2} \right]$$

(neglecting higher order terms of the expansion).

The condition for the applicability of this expansion being that $(E_n^1 + E_n^2) << kT$ where the perturbation energy is per particle. Hence the partition function,

$$Q = \sum_n e^{-E_n^0/kT} \left[1 + \frac{\sum_n e^{-E_n^0/kT} \cdot \frac{1}{kT} \left\{ -(E_n^1 + E_n^2) + \frac{(E_n^1 + E_n^2)^2}{2kT} \right\}}{\sum_n e^{-E_n^0/kT}} \right]$$

$$= Q_0 \left[1 + \frac{1}{Q_0} \sum_n e^{-E_n^0/kT} \cdot \frac{1}{kT} \left\{ -(E_n^1 + E_n^2) + \frac{(E_n^1 + E_n^2)^2}{2kT} \right\} \right] \ldots (3)$$

Q_0 being the partition function for the unperturbed system.

The equilibrium condition of the system which determines the coefficients of the potential energy is defined at constant pressure and not at constant volume as is usually done (Stern, 1958). This accounts for calling Q, the partition function at constant pressure, which gives the Gibb's function G through the relation $e^{-G/kT} = Q$.

Taking the logarithms of both sides of (3), multiplying by $-kT$ and using the expansion $ln\ (1+y) = y-y^2/2$ (neglecting higher order terms),

$$G = -kT \ln Q$$

$$= -kT \ln Q_0 - kT \cdot \frac{1}{Q_0} \sum_n e^{-E_n^0/kT} \cdot \frac{1}{kT} \left\{ -(E_n^1+E_n^2) + \frac{(E_n^1+E_n^2)^2}{2kT} \right\}$$

$$+ \frac{1}{2} kT \left[\frac{1}{Q_0} \sum_n e^{-E_n^0/kT} \cdot \frac{1}{kT} \left\{ -(E_n^1+E_n^2) + \frac{(E_n^1+E_n^2)^2}{2kT} \right\} \right]^2$$

$$= G_0 + \sum_n e^{(G_0-E_n^0)/kT} \cdot \left\{ (E_n^1+E_n^2) - \frac{(E_n^1+E_n^2)^2}{2kT} \right\}$$

$$+ \frac{1}{2kT} \left[\sum_n e^{(G_0-E_n^0)/kT} \cdot \left\{ (E_n^1+E_n^2) - \frac{(E_n^1+E_n^2)^2}{2kT} \right\} \right]^2$$

where G_0 is the Gibb's function for the unperturbed system.

As we are interested only in the 1st- and 2nd- order changes in the energy and the thermodynamic functions, (because we have only 1st- and 2nd- order corrections in the energy levels), G in that approximation becomes,

$$G = G_0 + \sum_n e^{(G_0-E_n^0)/kT} \cdot \left[(E_n^1+E_n^2) - \frac{(E_n^1)^2}{2kT} \right]$$

$$+ \frac{1}{2kT} \left[\sum_n e^{(G_0-E_n^0)/kT} \cdot E_n^1 \right]^2$$

$$= G_0 + \sum e^{(G_0-E_n^0)/kT} \cdot (E_n^1+E_n^2) - \frac{1}{2kT} \sum e^{(G_0-E_n^0)/kT} \cdot (E_n^1)^2$$

$$+ \frac{1}{2kT} \left[\sum_n e^{(G_0-E_n^0)/kT} \cdot E_n^1 \right]^2 \qquad \ldots \quad (4)$$

THERMODYNAMIC FUNCTIONS FOR A SIMPLE MODEL

For the model of a solid, it is considered as a collection of 3N linear anharmonic oscillators having the same frequency. N is the total number of atoms in the solid. The characteristic frequency ω is the Einstein frequency related to the characteristic temperature θ by the relation $\hbar\omega = k\theta$,

The Hamiltonian of a linear anharmonic oscillator, including cubic and quartic terms in displacement X can be written as,

$$H = \left(\frac{p^2}{2m} + \frac{1}{2} aX^2 \right) + (bX^3 + CX^4)$$

$$= H_0 + V \qquad \ldots (5)$$

where $H_0 = (p^2/2m + 1/2aX^2)$ is the unperturbed (Harmonic) Hamiltonian and $V = (bX^3 + cX^4)$ is the perturbing potential.

The perturbed energy levels E_n of such a perturbed system, using quantum mechanical perturbation theory, is the well known (Landau and Lifshitz, Q. M., 1958) result,

$$E_n = \left(n + \frac{1}{2} \right) \hbar\omega + C \cdot \frac{3}{4} \left(\frac{\hbar}{m\omega} \right)^2 (2n^2 + 2n + 1)$$

$$- b^2 \cdot \frac{15}{4\hbar w} \left(\frac{\hbar}{m\omega} \right)^3 \cdot \left(n^2 + n + \frac{11}{30} \right) \qquad \ldots (6)$$

The contribution to the 2nd-order correction has been considered only from the cubic term but not from the quartic term.

Having known the energy levels of the perturbed oscillator one can calculate the thermodynamic functions making use of the general formula (4). In the general notation,

$$\left.\begin{aligned} E_n^0 &= \left(n + \frac{1}{2} \right) \hbar\omega \\ E_n^1 &= C \cdot \frac{3}{2} \left(\frac{\hbar}{m\omega} \right)^2 \cdot \left(n^2 + n + \frac{1}{2} \right) \\ \text{aand} \quad E_n^2 &= - b^2 \cdot \frac{15}{4\hbar\omega} \left(\frac{\hbar}{m\omega} \right)^3 \left(n^2 + n + \frac{11}{30} \right) \end{aligned}\right\} \qquad \ldots (7)$$

As in the perturbed energy levels E_n, the contribution of cX^4 in the second order perturbation is not considered (which would have given otherwise, a term multiplied by c^2) for a consistent approximation the last two terms of (4) are dropped.

The expression for G (per oscillator) becomes then from (4),

$$G = G_0 + \sum e^{(G_0 - E_n^0)/kT} \cdot (E_n^1 + E_n^2)$$

which on putting E_n^1 and E_n^2 from (7) and collecting terms in powers of n reduces to,

$$G = G_0 + Ae^{(G_0 - \frac{1}{2}\hbar\omega)/kT} \cdot \left[\sum_n n^2 e^{-n \cdot \frac{\hbar\omega}{kT}} + \sum_n n e^{-n \frac{\hbar\omega}{kT}} \right]$$

$$+ B\, e^{(G_0 - \frac{1}{2}\hbar\omega)/kT} \cdot \sum_n e^{-n \cdot \frac{\hbar\omega}{kT}}$$

putting $\dfrac{\hbar\omega}{T} = x$

$$= G_0 + A\, e^{(G_0 - \frac{1}{2}\hbar\omega)/kT} \cdot [\Sigma n^2 e^{-nx} + \Sigma_n n e^{-nx}] + B$$

$$= G_0 + A \cdot \frac{1}{f(x)} [f''(x) - f'(x)] + B \qquad \ldots (8)$$

The primes on f denote differentiation with respect to x. The coefficients A and B, and the function $f(x)$ are,

$$\left.\begin{aligned} A &= C \cdot \frac{3}{2} \left(\frac{\hbar}{m\omega} \right)^2 - b^2 \cdot \frac{15}{4\hbar\omega} \left(\frac{\hbar}{m\omega} \right)^3 \\ B &= C \cdot \frac{3}{4} \left(\frac{\hbar}{m\omega} \right)^2 - b^2 \cdot \frac{11}{8\hbar\omega} \left(\frac{\hbar}{m\omega} \right)^3 \end{aligned}\right\} \qquad \ldots (9)$$

and $$f(x) = \sum_n e^{-nx} = \frac{e^x}{(e^x - 1)}$$

With the substitution of $f''(x)$ and $f'(x)$ of the function $f(x)$, defined in (9), the expression for G in (8) takes the form,

$$G = G_0 + 2A \cdot \frac{e^x}{(e^x - 1)^2} + B \qquad \ldots (10)$$

Having obtained the expression for the Gibb's function G, the specific heat at constant pressure C_p (per oscillator) can be calculated using the formula,

$$C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p$$

$$= -T \left(\frac{\partial^2 G_0}{\partial T^2} \right)_p + \frac{4A}{T} \cdot \frac{x(e^x + e^{2x})}{(e^x - 1)^3} - \frac{2A}{T} \cdot \frac{x^2(e^x + 4e^{2x} + e^{3x})}{(e^x - 1)^4}$$

$$= k \cdot \frac{x^2 \cdot e^x}{(e^x-1)^2} + \frac{4A}{T} \cdot \frac{x(e^x+e^{2x})}{(e^x-1)^3}$$

$$- \frac{2A}{T} \cdot \frac{x^2(e^x+4e^{2x}+e^{3x})}{(e^x-1)^4} \qquad \ldots (11)$$

This is the expression for the specific heat at constant pressure C_p (per oscillator).

Equations (10) and (11) give the Gibb's function G and the specific heat C_p for each oscillator or mode of vibration of the solid. For the model of the solid that is used here, to know G and C_p for the whole solid one has to multiply the expressions (10) and (11) by $3N$. It has already been mentioned earlier that the angular frequency ω is the characteristic (Einstein) frequency, related to the characteristic temperature θ by the relation $\hbar\omega = k\theta$.

To see whether the above development is on the right lines, one can take the limiting form of C_p at high temperatures i.e. when $kT >> \hbar\omega$ and compare the result with the classical expression. In this limit ($x << 1$),

$$C_p^{cl} = k - \frac{4A}{T} \cdot \frac{1}{x^2}$$

putting $$x = \frac{\hbar\omega}{kT}$$

and the value of A from (9)

$$= k - \frac{4k^2T}{(\hbar\omega)^2}\left[c \cdot \frac{3}{2} \left(\frac{\hbar}{m\omega}\right)^2 - b^2 \cdot \frac{15}{4\hbar\omega}\left(\frac{\hbar}{m\omega}\right)^3\right]$$

$$\omega = \sqrt{\frac{a}{m}}$$

$$= k\left[1 + \left(\frac{15b^2}{a^3} - \frac{6c}{a^2}\right) kT \right].$$

which agrees with the classical result (Peierls, 1955).

The validity of the above expressions (10) and (11) over a temperature range, is limited by the range of convergence of the quantum mechanical perturbation energy (2) and the range of convergence of the thermodynamic perturbation expansion (3). The results are not expected to be true at very low temperatures and that is the reason for believing that the Einstein model is good enough for the range of validity of the above expressions.

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